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(21) International Application Number: PCT/EP95/01414 (22) International Filing Date: 12 April 1995 (12.04.95) (30) Priority Data: PCT/EP94/01215 19 April 1994 (19.04.94) WO (34) Countries for which the regional or international application was filed: AT et al. 9426429.8 30 December 1994 (30.12.94) GB (71) Applicant (for all designated States except US): ROCKWOOL INTERNATIONAL A/S [DK/DK]; Hovedgaden 584, DK-2640 Hedehusene (DK). (72) Inventors; and (75) Inventors/Applicants (for US only): JENSEN, Soren, Lund [DK/DK]; Rudesovej 11, DK-2840 Holte (DK). CHRIS-TENSEN, Vermund, Rust [DK/DK]; Soager 11, DK-4000 Roskilde (DK). (74) Agent: GILL JENNINGS & EVERY; Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published <i>With international search report.</i>
(54) Title: MAN-MADE VITREOUS FIBRE WOOL (57) Abstract The production and physiological dissolution rate of mineral wool formed of MMV fibres containing 35-66 % SiO ₂ , up to 10 % Al ₂ O ₃ , 10-45 % CaO, 2-30 % MgO, up to 10 % FeO, 0-7 % Na ₂ O + K ₂ O and 0-10 % TiO ₂ is improved by including both P ₂ O ₅ and B ₂ O ₃ in the composition.		

MAN-MADE VITREOUS FIBRE WOOL

The present invention relates to man-made vitreous fibre (MMVF) wool containing iron and a relatively high amount of alkaline earth metals, and a low amount of alkali metals, conventionally known as stone, slag or basalt wool.

Various types of MMV fibres are known.

It is known, in the manufacture of traditional glass fibres, to include in the glass melt components which provide boron oxide (borate). This can improve the glass and the glass melt. However, borate-containing raw materials are expensive and are normally not added at all if possible, especially when the product contains iron and has low alkali and high alkaline earth content, as in conventional rock, stone and slag melts.

Glass wool products usually have a relatively high content of alkali metal (often above 13% $\text{Na}_2\text{O} + \text{K}_2\text{O}$). In this specification all analyses are expressed by weight of total composition measured as oxides. Glass filament and glass wool are usually free of iron but often also contain boron. Typically they contain less than 7% Al_2O_3 . However E-Glass is a filamentary or other non-wool product and can have high aluminium and low or zero alkali metal. For instance JP-A-50090719 describes an E-Glass containing 15-16% Al_2O_3 , 9.5-10.5% B_2O_3 and 5% P_2O_5 . It is free of iron and sodium.

Glass fibres are described in EP-A-9418 which can have a wide range of optional components including, inter alia, iron, boron and phosphorous. None of the exemplified compositions contain both boron and phosphorous and they all have above 13% alkali metal oxide.

WO93/07741 describes fibres containing 0 to 4% P_2O_5 , above 13% Na_2O , and up to 8% Al_2O_3 for use in horticulture. B_2O_3 can be present but the total amount of impurities (including any B_2O_3 which is included) must be not above 1%.

Glass wool is described in EP-A-412878 which has high alkali metal content (above 13%) and which contains borate. It is free of iron. Phosphorous is an optional component.

increases the risk of the melt (which contains iron and little or no alkali metal and low aluminium) undergoing phase separation and crystallisation. This leads to the formation and accumulation of solid or slag material in or on the apparatus being used for forming the melt and converting the melt to fibres, and can cause increased amount of shot formation during the fibre-formation process, reduced material efficiency and higher costs.

It would therefore be desirable to form MMVF wool having solubility characteristics of the type which would be expected in such wool from the use of relatively high phosphorus content while avoiding the manufacturing problems associated with relatively high phosphorous contents.

These problems tend to increase as the content of phosphate in the melt increases. For instance difficulties may arise as the content of phosphate increases beyond 5%. It may be possible with some furnaces to use up to 10% phosphate but in general for processing purposes it is undesirable to include more than this.

However, even at low levels of alumina, and in particular when it is not possible to provide a melt having very low levels of alumina, dissolution rates of the fibres are not as high as may be desirable at these levels of phosphate.

Therefore it would be desirable to improve the solubility of MMV fibres in the physiological medium without the necessity for using amounts of phosphate which lead to processing problems.

Fibres containing phosphorus and boron are mentioned in WO94/23801, from which this application claims priority.

According to the invention there is provided MMVF wool formed of fibres formed from a composition comprising, by weight of oxides (with iron expressed as FeO):

SiO ₂	35-66%
Al ₂ O ₃	up to 10%
CaO	10-45%

method described in Environmental Health Perspectives, Vol. 102, Supplement 5, October 1994, pages 83-86.

The wool of the invention may be provided in any known way. According to the invention we also provide a process of production of MMVF wool formed of fibres having a composition as defined above, the process comprising

providing raw materials to give the composition,
providing a furnace,
10 placing the raw materials in the furnace and heating them to a temperature between 1,400°C and 1,600°C to produce a melt,
fiberising the melt, and
collecting the fibres as a wool.

15 In this process we find all the advantages in processing characteristics discussed above. Preferably the wool of the invention are made by this process of the invention.

In the process of the invention the raw materials used to produce the melt may be any known raw materials which give the constituents of the composition. For instance, raw materials which may be used include diabase, cement, clay, olivine sand, silica sand, waste foundry sand, rasorite, colemanite and other boron-containing materials, converter slag, blast-furnace slag, electric arc furnace slag, iron oxide, waste stone wool, waste asbestos, lime, soda, glass waste, dolomite, bauxite, iron silicate, kaoline, calcium phosphate, quartz sand and other known melt ingredients.

30 The melt composition and hence the composition of the produced fibres preferably comprises at least 45%, often at least 47 or 48%, SiO_2 . The amount is usually below 64 or 65%, preferably below 60%. Often the amount of SiO_2 is from 53.5 to 64%.

35 The composition preferably has a low alumina content, generally below 6% and preferably below 4%. In general it is very expensive to provide raw materials which contain no

below) can give good results at economic cost but amounts up to 7 or 8% are sometimes preferred. The amount must be sufficient to give a useful effect and so is normally above 0.5 or 1% and preferably it is at least 3%. The amount of B_2O_3 is usually below the amount of P_2O_5 for reasons of economy.

TiO_2 is optional. If present, its amount is usually 0.1 to 2%. The melt composition may additionally comprise 0 to 20% of other ingredients, for instance BaO , ZnO , ZrO_2 , F_2 , MnO , Li_2O , SrO . The total amount of other ingredients is usually not more than 5%, or at most 10%.

The composition of the melt and of the fibres particularly preferably comprises:

SiO_2 45-64%, preferably 47-60 or 48-60%
15 Al_2O_3 0.5 to 4%
 CaO 10-35%,
 MgO 5-20%, preferably 5-15 or 7-15%
 FeO 1-10%, preferably 1 to 9%
 Na_2O 0 to 4%
20 K_2O 0 to 2%
 TiO_2 0 to 2%
 P_2O_5 at least 0.5% but preferably below 5%
 B_2O_3 at least 0.5% but preferably below 5%
other elements 0 to 5%

25 all percentages being by weight of total composition and iron oxides being measured as FeO .

The raw materials are placed in a furnace where they are heated to a temperature between 1,400°C and 1,600°C in order to produce a melt. In general, they are heated to at least 1,450°C, preferably between 1,450 and 1,540°C, generally around 1,480°C to 1,520°C.

The furnaces which can be used in the invention for forming the melt which is to be fiberised include cupola furnaces, oil and/or gas fired shaft or tank furnaces or electric furnaces. In these furnaces the invention is particularly advantageous, although the composition also

growing medium, for sound or heat insulation and protection, for fire resistance and protection and as a filler or reinforcement.

The following are examples of suitable compositions,
5 (determined by X-ray fluorescence analysis and measured as weight %) and their dissolution rate at pH 7.5 in nm per day. Each composition can be melted in a cupola furnace and fiberised as in WO92/06047.

10 Compositions 1, 2, 3 and 4 are within the invention while 1A, 1B, 2A, 3A and 4A are approximate comparisons and show that omitting the boron reduces dissolution rate. The comparative, borate free, compositions tend to slag formation, especially with the higher phosphorous contents.

CLAIMS

1. Mineral wool formed of MMV fibres having a composition, expressed as oxides by weight of total composition, which is

5	SiO ₂	35-66%
	Al ₂ O ₃	up to 10%
	CaO	10-45%
	MgO	2-30%
	FeO	up to 10%

10	Na ₂ O + K ₂ O	0-7%
	TiO ₂	0-10%

P₂O₅ + B₂O₃ and other elements up to 20%

and which includes both P₂O₅ and B₂O₃.

2. A wool according to claim 1 in which Al₂O₃ is up to 4% and each of P₂O₅ and B₂O₃ is up to 10%.

3. A wool according to claim 1 or claim 2 in which SiO₂ is 53.5 to 65%, CaO is 10-30%, MgO is 5 to 20%, and FeO is up to 9%.

4. A wool according to claim 1 in which the composition includes

20	SiO ₂	53.5-64% by weight
	Al ₂ O ₃	up to 4% by weight
	CaO	10-20% by weight
	MgO	10-20% by weight
25	FeO	6.5-9% by weight

P₂O₅ + B₂O₃ up to 20% by weight and each is up to 10%.

5. A wool according to claim 1 in which the composition includes

30	SiO ₂	53.5-65% by weight
	Al ₂ O ₃	up to 4% by weight
	CaO	15-30% by weight
	MgO	5-15% by weight
	FeO	up to 4% by weight

P₂O₅ + B₂O₃ up to 20% by weight and each is up to 10%.

6. A wool according to claim 1 in which the composition includes P₂O₅ and B₂O₃ and

35	SiO ₂	45 to 60%
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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 95/01414

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 009 418 (OY PARTEK AB) 2 April 1980 cited in the application see claim 1 ---	1-11
A	DATABASE WPI Section Ch, Week 7710 Derwent Publications Ltd., London, GB; Class F, AN 77-16933Y & JP,A,50 090 719 (NIHON MUKI ZAIRYO) , 21 July 1975 cited in the application see abstract ---	1-11
A	EP,A,0 247 817 (PFIZER INC.) 2 December 1987 see page 2, line 58 - page 3, line 12 --- -/--	1-11

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

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3 August 1995

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